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SYNTHESIS AND CRYSTAL STRUCTURE OF POLY-TRIVINYLTINFERROCENOATE

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Summary

Binuclear complexes of formula $C_5H_{15}FeC_5H_4COOSn(CH{=}CH_2)_3$ (I), $C_5H_5FeC_5H_4COOSnPh_3$ (II) and $Ph_3GeCOOSnPh_3$ (III) have been prepared and characterized by IR spectra. The polymeric structure of solid $C_5H_5FeC_5H_4COOSn(CH{=}CH_2)_3$ has been established by X-ray crystallography. The crystals are monoclinic, space group $P2_1/a$, with a 15.105(5), b 10.030(4), c 11.402(4) Å, and β 104.06(4)°. In this compound the tin atoms are five-coordinate trigonal bipiramidal, with the vinyl groups equatorial and two apical oxygen atoms from bridging carboxylato groups. The resulting structure is a linear polymer with Sn—O bond lengths of 2.12 and 2.42 Å. The spectra indicate that similar polymeric structure exist also for compounds II and III in the solid state, whereas an equilibrium monomer $\rightleftharpoons$ dimer seems to be present in $CHCl_3$ solution for the compound III.

Introduction

The structure and bonding of triorganotin acylates have been the subject of many studies [1—4], which indicate that trialkyltin carbonylates with small alkyl groups have polymeric structures in the solid state, with planar SnC_3 groups and bridging acyloxy groups, whereas they are ester-like monomers in dilute solution.

Generally, formation of the polymeric structure is impeded by steric hindrance of bulky groups attached to the metal, [5] while the influence of bulky groups bonded to the —COO is not yet well established. Because of this and with the aim of determining whether the structural properties of the triorganotin acylates can be affected by the additional presence of a second metal atom, three binuclear complexes, of formula $C_5H_5FeC_5H_4COOSn(CH{=}CH_2)_3$ (I), $C_5H_5FeC_5H_4COOSnPh_3$ (II), and $Ph_3GeCOOSnPh_3$ (III) were synthesized and characterized.

In principle there is the possibility for the bulky carboxylate ligand, potentially bidentate, to be present in the ester-like form in monomeric species in which the tin atoms are four-coordinate (the $\nu_{as}(COO)$ in these compounds are generally in the range 1650—1730 cm^{-1}), or as bridging group in polymeric species in which the tin atoms are five-coordinate, when the $\nu_{as}(COO)$ generally fall in the range 1530—1650 cm^{-1} [2,3,6,7]. Because of the large increase in the $\nu_{as}(COO)$ (70 to 100 cm^{-1}) upon solution depolymerization of the species, IR spectra are a key feature in establishing the polymeric nature of the solid from identification of the bidentate carboxylate groups. However, in the binuclear complexes examined, the position of the $\nu_{as}(COO)$ bands in solution, in which they can reasonably be regarded as monomeric species, is not appreciably different from that of the solid (see Table 1) for compound I and II. Thus the structure of trivinyltin ferrocenoate, which gives particularly well formed crystals, was definitively determined by X-ray analysis.

Experimental

Trivinyltinferrocenoate. To 1.224 g (5.32 mmol) of ferrocenecarboxylic acid (Alfa Inorganics) was added 10.18 ml of 0.5226 *M* sodium hydroxide (5.32 mmol) with gentle heating to effect solution. The water was removed under reduced pressure leaving 5.92 mmol of sodium ferrocenoate.

A mixture of sodium ferrocenoate (4 mmol), trivinyltin acetate (4 mmol) (prepared as previously reported [8]) and 50 ml of dry benzene was refluxed for 2 h. The insoluble sodium acetate formed was filtered off and the solvent was removed in a rotary evaporator leaving 1.6 g of red-orange solid, m.p. 146—148° C. Upon recrystallization from benzene-petroleum ether, this gave 1,2 g

TABLE 1

IR FREQUENCIES, MELTING POINTS AND MOLECULAR WEIGHTS OF BINUCLEAR TRIORGANOTIN COMPLEXES

Compound		$\nu_{as}(COO)$ (cm^{-1})		M.p. (°C)	Mol. wt.	
		solid [a]	solution		calcd.	found
I	$C_5H_5FeC_5H_4COOSn(CH{=}CH_2)_3$	1565	1615 [b]	152	428	605
II	$C_5H_5FeC_5H_5COOSnPh_3$	1605	1620 [b]	123	579	750
III	$Ph_3GeCOOSnPh_3$	1585	1585 [c] 1710 [c]	185	698	782

[a] Nujol mull. [b] Carbon tetrachloride solution. [c] Chloroform solution.

(70%) of trivinyltin ferrocenoate, m.p. 152°C (Found C, 47.0; H, 4.3, $C_{17}H_{18}O_2FeSn$ calcd.: C, 47.6; H, 4.2%). Mol.wt.: calcd. 428.5, found 605.

Triphenyltin ferrocenoate. A solution of 0.671 g (2.66 mmol) of sodium ferrocenoate in 30 ml of benzene was refluxed with 0.448 g (2.66 mmol) of triphenyltin chloride for 2 hours. The white solid (NaCl) which separated was filtered off, and the solvent removed, leaving a rubber-solid which, after agitation with n-hexane for ten hours gave 0.450 g (29%) of triphenyltin ferrocenoate as a powder, m.p. 123°C (Found C, 60.6; H, 4.1, $C_{29}H_{24}O_2FeSn$ calcd.: C, 60.1; H, 4.2%). Mol.wt.: calcd. 578.7, found 750.

Triphenyltin triphenylgermanecarboxylate. To 0.53 g (1.52 mmol) of triphenylgermanecarboxylic acid prepared as previously reported [9,10] was added 10.85 ml of 0.14 *M* sodium hydroxide (1.52 mmol) with gentle heating to effect solution. The water was removed under reduced pressure. To the white solid formed was added a solution of 0.61 g triphenyltin chloride (1.58 mmol) in 30 ml of benzene. The mixture was refluxed for 2 hours, filtered, and the benzene removed under reduced pressure. The white solid formed was recrystallized from benzene and petroleum ether. A total of 0.57 g (54%) of triphenyltin triphenylgermane/carboxylate, m.p. 185°C, was isolated (Found C, 64.8; H, 4.2, $C_{37}H_{30}O_2GeSn$ calcd.: C, 63.7; H, 4.3%). Mol.wt.: calcd. 697.9, found 782. The infrared spectrum was characteristic of an ester and particularly shows characteristic absorptions of phenyl bonded to tin at 1070 cm^{-1} and of phenyl bonded to germanium at 1085 cm^{-1} [11,12].

Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrometer, calibrated with a polystyrene film in the range 4000—250 cm^{-1}, in Nujol, in $CHCl_3$ and CCl_4 with KBr or CsI optics.

Molecular weights were determined with a Mechrolab 302B vapor phase osmometer at 37° C in benzene solution.

Intensity data

Recrystallization by slowly evaporating the solvent from a benzene solution of trivinyltin ferrocenoate gave, after a week, well-formed crystals suitable for X-ray studies. A well formed prismatic fragment of approximate dimensions 0.10 × 0.10 × 0.18 mm was mounted on a glass fibre with epoxy adhesive. Preliminary precession and Weissenberg photography established that the crystals were monoclinic, belonging to space group $P2_1/a$. All subsequent X-ray experimental work was performed on a Philips PW 1100 four-circle automated diffractometer using Mo-K_α radiation. The unit cell parameters were obtained by a least-squares refinement of 25 carefully determined angular settings. Crystal data are summarized in Table 2. Intensities were measured by the $2\theta - \omega$ scan method in the range $2\theta \leqslant 50°$ with a scan rate of 2° min^{-1}. Two standard reflections, monitored before every 100 measurements, were constant within counting statistics. All data were corrected for Lorentz and polarization. No absorption correction was applied.

The asymmetric unit comprises one binuclear molecule. The positions of the two heavy atoms were determined from a three-dimensional Patterson map, and the whole structure was then obtained by successive Fourier syntheses phased on least-squares refined positional and isotropic thermal parameters.

TABLE 2

CRYSTAL DATA

$C_{17}H_{18}O_2FeSn$	FW 428.5
Crystal description	red-orange prisms
Systematic absences	$h0l$ $h = 2n$ $0k0$ $k = 2n$
System	monoclinic
Space group	$P2_1/a(C^5_{2h})$
General positions	$\pm(x, y, z; 1/2 + x, 1/2 - y, z)$
Cell dimensions	a 15.105(5) Å b 10.030(4) Å c 11.402(4) Å β 104.06(4)° V 1676 Å^3
Density	obs. 1.70 g cm^{-3} (flotation, calcd. 1.70 g cm^{-3} for $Z = 4$)
μ(Mo-K_α)	24.9 cm^{-1}
Total number of intensities measured	3646
"Unobserved" $I < 3\sigma(I)$	1282
Final R factor	0.05

The function $\Sigma w(F_0 - F_c)^2$ was minimized with $w = 1$ and with structure factors calculated using form factors for neutral atoms taken from Cromer and Waber [13]. Those of Fe and Sn were corrected for the real and imaginary parts of the anomalous dispersion [14]. Introducing anisotropy reduced the conventional R factor to the value of 5.2% when the maximum shift of the positional parameters was 0.2σ.

A final three-dimensional difference synthesis showed no significant anomaly, and revealed the position of some but not all the hydrogen atoms. Therefore only the ring hydrogen atoms were introduced, in calculated positions. The final conventional R factor was 5%. Calculations were performed using the X-ray '73 program system [15]. A list of observed and calculated structure factors is available from the author. The final atomic coordinates are listed in Table 3. Interatomic bond distances and angles are reported in Table 4. Least-squares planes through selected atomic groupings are in Table 5.

Description of the structure

The complex crystallizes as a one-dimensional polymer along the needle axis with the carboxylato groups acting to bridge the tin units, as schematically shown in Fig. 1.

The tin atoms in the chain are not colinear but, as shown in Fig. 2, are arranged alternately along helical chains around the screw axes of the cell. A projection of the structure down the c axis is shown in Fig. 3 together with the numbering scheme.

The tin atoms are in an axially-distorted, trigonal-bipyramidal arrangement with the vinyl groups equatorial, and the oxygen atoms axial. Slight distortions from regular D_{3h} symmetry of the coordination polyhedron can be seen in the axial O—Sn—O angle of 172°, which is probably consistent with the occurrence of intermolecular coordination, as well within the equatorial plane where the

TABLE 3

ATOMIC COORDINATES

	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$
Sn	0.7740(1)	0.3267(1)	0.0572(1)
Fe	0.8909(1)	0.7349(1)	0.4056(1)
O(1)	0.7975(5)	0.6445(6)	0.0710(6)
O(2)	0.8506(5)	0.4682(5)	0.1786(5)
C(1)	0.7708(7)	0.8122(12)	0.4202(10)
C(2)	0.7652(7)	0.6744(13)	0.4087(11)
C(3)	0.8286(9)	0.6170(12)	0.5041(12)
C(4)	0.8742(9)	0.7154(16)	0.5759(10)
C(5)	0.8399(8)	0.8404(13)	0.5247(11)
C(6)	0.9799(5)	0.6173(10)	0.3485(8)
C(7)	1.0256(7)	0.7248(13)	0.4149(10)
C(8)	0.9900(7)	0.8445(12)	0.3586(10)
C(9)	0.9194(8)	0.8141(9)	0.2553(9)
C(10)	0.9137(6)	0.6699(8)	0.2496(8)
C(11)	0.8480(6)	0.5925(8)	0.1579(8)
C(12)	0.8390(12)	0.3569(14)	−0.0835(12)
C(13)	0.8266(9)	0.1720(11)	0.1775(12)
C(14)	0.6450(14)	0.3754(18)	0.0492(14)
C(15)	0.8458(14)	0.1734(15)	0.2845(14)
C(16)	0.8983(16)	0.4228(28)	−0.0973(20)
C(17)	0.6066(21)	0.4310(32)	0.1154(23)

Calculated coordinates of the rings hydrogen atoms assuming a C—H bond length of 0.98 Å.

	x	y	$z($
H(C1)	0.7337	0.8776	0.3656
H(C2)	0.7233	0.6256	0.3438
H(C3)	0.8388	0.5210	0.5174
H(C4)	0.9221	0.7026	0.6501
H(C5)	0.8605	0.9290	0.5562
H(C6)	0.9916	0.5226	0.3573
H(C7)	1.0747	0.7179	0.4885
H(C8)	1.0106	0.9344	0.3864
H(C9)	0.8822	0.8777	0.1990

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	86	46	67	−7	10	3
Fe	55	53	71	−3	18	−9
O(1)	106	52	72	−7	4	−4
O(2)	122	38	74	6	−5	−6
C(1)	76	97	96	9	33	−17
C(2)	67	107	118	−14	45	−3
C(3)	90	104	111	−1	48	12
C(4)	109	145	82	12	41	2
C(5)	95	119	105	−1	54	−41
C(6)	52	100	75	14	14	−16
C(7)	58	118	110	−18	29	−35
C(8)	76	95	104	−43	33	−20
C(9)	114	63	86	−30	51	−16
C(10)	68	52	78	−7	30	−17
C(11)	78	50	63	7	19	−3
C(12)	129	118	90	−43	18	17
C(13)	142	62	88	−7	3	2
C(14)	178	173	88	100	13	−36
C(15)	256	104	96	7	−4	3
C(16)	171	310	185	−32	91	−60
C(17)	228	328	167	44	44	10

Temperature factors of non-hydrogen atoms (X 10^3)

The anisotropic temperature factor is given by $\exp\{-2\pi^2(a^{\star 2}h^2U_{11} + b^{\star 2}k^2U_{22} + c^{\star 2}l^2U_{33} + a^{\star}b^{\star}hkU_{12} + a^{\star}c^{\star}hlU_{13} + b^{\star}c^{\star}klU_{23})\}$

TABLE 4

BOND DISTANCES (Å)

Sn—O(1)	2.42(1)	Fe—C(1)	2.02(1)
Sn—O(2)	2.12(1)	Fe—C(2)	2.00(1)
Sn—C(12)	2.10(2)	Fe—C(3)	2.01(1)
Sn—C(13)	2.10(1)	Fe—C(4)	2.03(1)
Sn—C(14)	2.16(2)	Fe—C(5)	2.02(1)
C(11)—C(10)	1.47(1)	Fe—C(6)	2.01(1)
C(11)—O(1)	1.21(1)	Fe—C(7)	2.01(1)
C(11)—O(2)	1.27(1)	Fe—C(8)	2.03(1)
C(12)—C(15)	1.15(4)	Fe—C(9)	2.03(1)
C(13)—C(16)	1.18(3)	Fe—C(10)	2.00(1)
C(14)—C(17)	1.20(3)		
C(1)—C(2)	1.39(2)	C(6)—C(7)	1.40(1)
C(2)—C(3)	1.39(2)	C(7)—C(8)	1.40(2)
C(3)—C(4)	1.36(2)	C(8)—C(9)	1.42(1)
C(4)—C(5)	1.43(2)	C(9)—C(10)	1.45(1)
C(5)—C(1)	1.41(1)	C(10)—C(6)	1.41(1)

BOND ANGLES (°) [a]

O(1)—Sn—O(2)	172.5(2)	Sn—O(1)—C(11)	156(1)
C(12)—Sn—C(13)	116(1)	Sn—O(2)—C(11)	123(1)
C(12)—Sn—C(14)	127(1)	O(1)—C(11)—O(2)	124(1)
C(13)—Sn—C(14)	114(1)	O(1)—C(11)—C(10)	122(1)
O(1)—Sn—C(12)	83(1)	O(2)—C(11)—C(10)	114(1)
O(1)—Sn—C(13)	83(1)	C(6)—C(10)—C(11)	126(1)
O(1)—Sn—C(14)	86(1)	C(9)—C(10)—C(11)	125(1)
O(2)—Sn—C(12)	97(1)		
O(2)—Sn—C(13)	90(1)		
O(2)—Sn—C(14)	100(1)		

[a] Bond angles in the rings are all between 107° and 109° with a mean value of 108°.

TABLE 5

LEAST-SQUARES PLANES AND DISTANCES (Å) OF ATOMS FROM THE PLANES

Plane I	Sn, C(12), C(13), C(14) $5.07X + 7.42Y + 5.53Z = 6.50$ Å (Sn 0.16, C(12) —0.06, C(13) —0.05, C(14) —0.06)
Plane II	C(1) to C(5) $12.68X + 0.14Y - 8.33Z = 6.39$ Å (Fe [a] —1.62, carbon atoms are coplanar, the greatest deviation from the plane is 0.005 Å)
Plane III	C(6) to C(10) $12.54X - 0.18Y - 8.46Z = 9.23$ Å (Fe [a] —1.62, carbon atoms are coplanar, the greatest deviation from the plane being 0.04 Å)
Plane IV	O(1), O(2), C(11) $13.74X - 0.88Y - 7.01Z = 10.02$ Å

The equation of a plane is $PX + QY + RZ = S$ with coordinates referred to the crystallographic axes.

ANGLES BETWEEN THE PLANES

Plane	Angle (°)	Plane	Angle (°)
I—II	89	II—III	2
I—III	87	II—IV	11
I—IV	90	III—IV	11

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[a] Atom not used in the plane calculation.

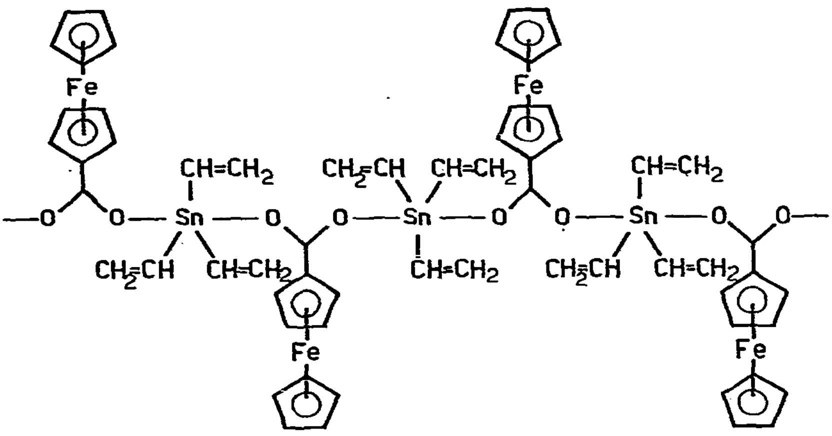

Fig. 1. Bridging scheme in Poly-trivinyltinferrocenoate.

bonded carbon atoms subtend angles of 114°, 116°, and 127°. Tin—carbon distances (2.10 to 2.16 Å) have comparable values which agree with those generally found in the literature. In contrast the two tin—oxygen bonds are distinctly dissimilar and this feature may play an important role in the adjustment of bond angle with the groups attached to tin. All the O(1)—Sn—C(equatorial) angles are acute, whereas the corresponding O(2)—Sn—C angles are obtuse or 90°; accordingly the central atom is significantly displaced from the equatorial mean plane toward O(1) (Table 5). The short Sn—O(2) distance of 2.12 Å agree well with the values of 2.14 Å found in triphenyltin formate [16] and with the 2.17 Å in trivinyltin trichloroacetate [17] whose polymeric structures show some analogies, but the Sn—O(1) distance of 2.42 Å is shorter than the corresponding bridging oxygen distances in the same compounds (2.65 and 2.49 Å). The carboxylate group, which is exactly perpendicular [18] to the equatorial plane, has the *syn-anti* configuration [18] observed in polymeric organotin compounds and the angles at the oxygen atoms (123° and 156°) compare well with those found in trivinyltintrichloroacetate (123° and 157°). The two carbon—oxygen bonds are not equivalent, the C=O double bond being associated with the oxygen atom O(1), which makes a weaker bond with tin. In addition the O(2)—C(11)—C(10) angle of 114° is about 10° smaller than the other two angles at C(11), and this in accord with a higher electronic density along the C(11)—O(1) bond.

Both cyclopentadienyl rings are quite planar and π-bonded to the iron(II) ion, which is equidistant from these planes. It is noteworthy that the two five-membered rings are eclipsed, as in ruthenocene, whilst they are staggered in ferrocene. Deviations from this configuration were previously observed in biferrocenyl [19] where the rings are neither fully eclipsed nor fully staggered but somewhere between these extremes, and in -keto-1,1′-trimethyleneferrocene [20], where they are more nearly eclipsed. This suggests that the energy barrier between the two configurations is not high, and that intermolecular packing forces are probably involved in determining it. Bridging causes no

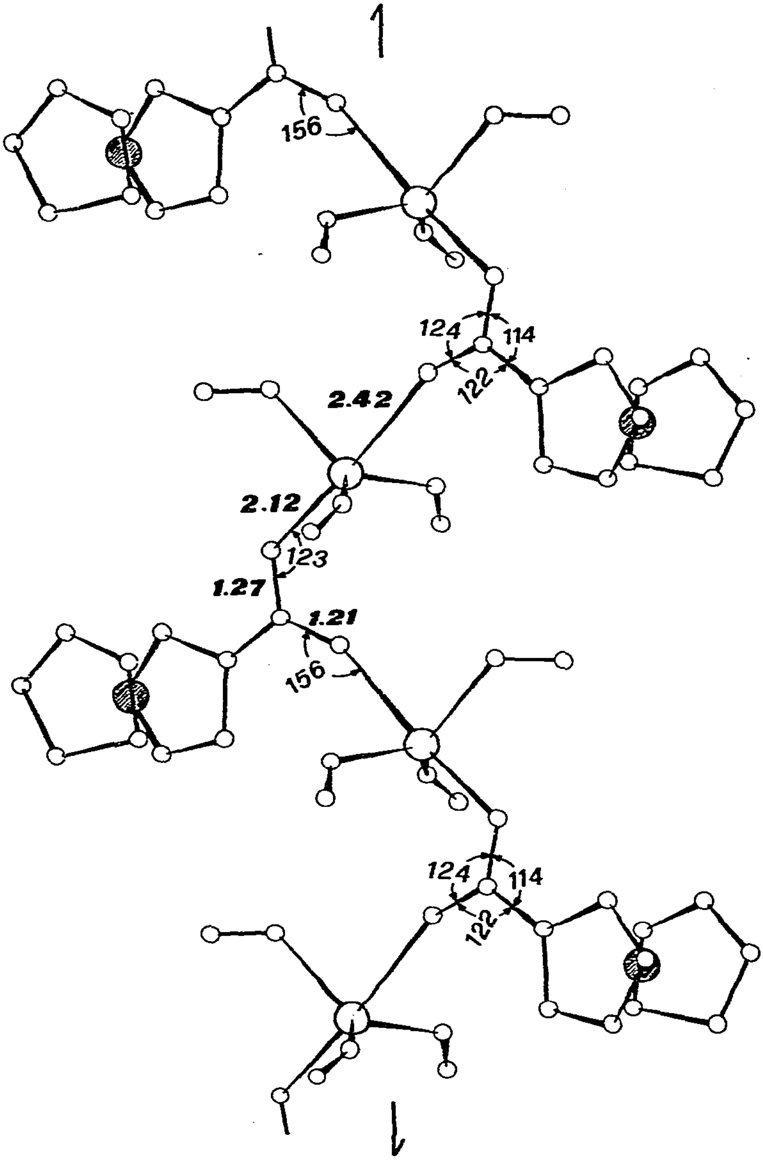

Fig. 2. Helical chain arrangement in Poly-trivinyltinferrocenoate.

appreciable tilting of the cyclopentadienyl rings so they can be considered parallel as in the parent compound, ferrocene. The dihedral angle between them is 2°. All Fe—C bond lengths are in the range 2.00—2.03 Å. Bond lengths in the rings are normal. Bond lengths in the vinyl groups are of little significance because of the rather limited accuracy of the positions of the terminal carbon atoms, as indicated by the relatively high temperature factors. The iron atom makes contacts of 3.84 Å and 3.67 Å with O(1) and O(2), respectively. No other significant contact distances are present in the structure.

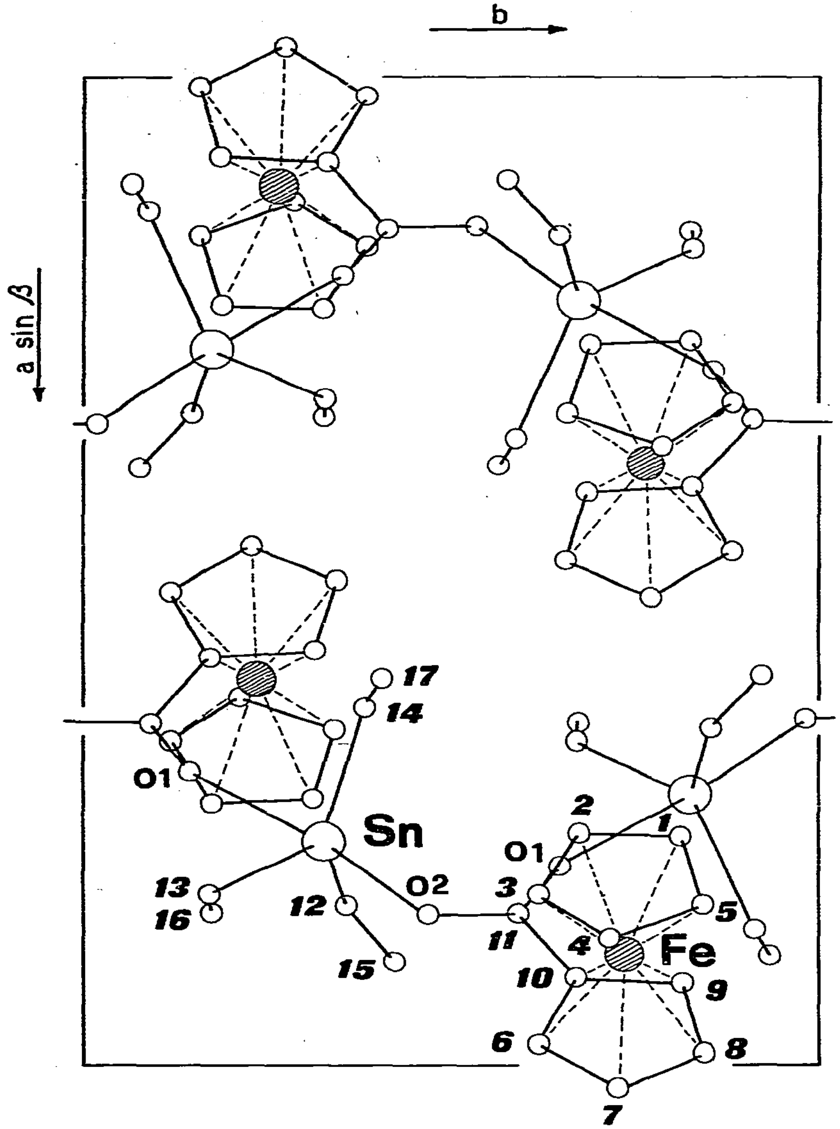

Fig. 3. Projection of the structure down the c axis.

Comparison of the ν_{as}(COO) stretching frequencies (Table 1) suggests that a polymeric structure similar to that found by X-ray analysis in I must be postulated also for II and III in the solid state. On solution the bands undergo moderate shifts toward higher frequencies in I and II, indicating that these compounds are probably present as monomers in solution. In contrast III exhibits two peaks in solution: one centred at 1585 cm^{-1} (as in the solid), which was attributed to a bridging carboxylato group, the second at 1710 cm^{-1} which is typical of an organic ester [21]. Therefore the existence of monomer–dimer equilibrium must be postulated for this compound in chloroform solution.

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